A NEW SOLID-STATE ION-SELECTIVE ELECTRODE SENSITIVE TO PB(II) IONS

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ABSTRACT

A new solid-state membrane ion-selective electrode sensitive to Pb(II) ions was developed. Two different methods based on two different sulfide preparation techniques were employed to make up the membrane of the electrode. The electrodes with the membranes prepared by these two methods did not show any appreciable difference in performance. The proposed electrode exhibited a Nernstian slope of 28.3 ± 0.2 mV/pPb over a wide working range from 1.0×10^{-1} to 1.0×10^{-5} M. It has a fast response time (< 10 s), a satisfactory reproducibility and a relatively long lifetime (> a year) without any considerable divergence in potential. The selectivity coefficients of thirteen cations were determined by the fixed interference method and the electrode showed a fairly good selectivity to Pb^{2+} ion in comparison to other common cations, namely Cd^{2+}, Cu^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Mn^{2+}, Zn^{2+} and Sr^{2+}. It was found that only Ag^{+} and Hg^{2+} had an interfering effect. The influence of pH was studied and the potential response was independent of the pH of the test solutions in the range 3.5-6.0. It was successfully used as an indicator electrode in the potentiometric titration of lead ions with EDTA to determine the lead contents of a standard lead solution and standard lead samples. The results obtained were compared with

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those obtained by the use of commercial Pb(II)-selective electrode. Such a Pb(II)-selective electrode, proposed here, can be constructed for commercial purposes.

Keywords: Ion-selective electrodes; Lead(II) determination; Solid-state membrane; potentiometry

1. INTRODUCTION

Measuring and controlling the concentration of heavy metals has become a quite essential research area mainly due to the material's toxic nature from the environmental point of view /1/. Lead is one of the most toxic elements. It causes poisoning, cancer, brain damage and also it can cause mental retardation and semi permanent brain damage in young children. It has the ability to replace calcium in bone to form sites for long-term release /2/. Because of the increased use of lead and its compounds in various industrial processes and its serious hazardous effect on human health, the determination of lead in various industrial, environmental and biochemical samples became an important goal all over the world.

Many sophisticated analytical techniques such as spectrophotometry, solvent extraction, carrier mediated transport, etc. have been reported for the determination of heavy metals because of the growing environmental and clinical problems. However, they are time consuming, involving multiple sample manipulations, too expensive for many analytical laboratories and they also require large infrastructure back up /3/. Hence, there has been a profound development in devices for rapid, accurate, low cost and nondestructive method of analysis in a given sample. As a result of extensive research in this area, the development of chemical sensors such as ion-selective electrodes has received widespread attention over the last few decades due to the urgent need for selective potentiometric determination of heavy metals such as lead, mercury, nickel, silver and cadmium. A number of ion-selective electrodes for many alkali, alkaline earth and some heavy and transition metal ions are now commercially available. Moreover, the number of Pb(II) sensitive solid-state membrane ion-selective electrodes is limited in literature /4-8/. The electrodes reported are mainly neutral carrier based polymer membrane electrodes /2, 9-34/ and modified carbon paste electrodes

/35/. However, these electrodes have certain disadvantages such as short lifetimes, leakage and rupture of the membrane. Furthermore, as they contain internal filling solution, their prolonged use may create problems such as surface contamination, which is very difficult to eliminate /36/.

In literature, to get a disc shaped membrane, most of the solid-state electrode membranes were prepared by applying high pressure at different temperatures for a long time /37-40/. This process generally affects the performance of the membrane. This paper presents a Pb(II)-selective solid-state membrane electrode constructed by the use of a mixture of PbS-Ag_2S which was prepared by a new technique that does not need any pressing process to get a disc shaped membrane. The electrode developed exhibited significantly high selectivity to Pb(II) ions over several alkali, alkaline earth and some heavy and transition metal ions and was successfully used in the determination of Pb(II).

2. EXPERIMENTAL

2.1. Apparatus

All potentiometric measurements were made at 25±1 °C; a Consort pH/mV meter (model C863) and Ingold U402-S7/120 glass electrode were used for pH measurements. In order to compare the application results of the proposed electrode with the results obtained from the commercially available lead electrode, an Orion specific ion electrode model 94-82A was used.

2.2. Reagents and materials

All the chemicals used in this study were of analytical reagent grade and used without further purification. 0.1 M stock solutions of the metal ions were prepared. The experimental solutions were prepared with the dilution of the stock solutions with ultra pure deionized water obtained from ELGA Purelab Classic Ultra pure water System. $Hg(NO_3)_2$ (99.0 %), $AgNO_3$ (99.8 %), $Al(NO_3)_3$ (99.8 %), $Cr(NO_3)_3$ (99.0 %), $Ni(NO_3)_2$ (97.0 %), $Pb(NO_3)_2$ (98.5 %), $Co(NO_3)_2$ (99.0 %), $Cu(NO_3)_2$ (97.0 %), NaOH (97.0 %), HNO_3 (65 %; d = 1.42 kg/L), EDTA (98.0 %), KNO_3 (99.0 %), $Ca(NO_3)_2$ (98.0 %), $Fe(NO_3)_3$ (99.0 %), $NaNO_3$ (99.9 %), $Mg(NO_3)_2$ (98.0 %) and thioacetamide (99 %) were purchased from the Merck company, HCl (37 %; d = 1.19 kg/L) from the Riedel-De-Haen company, Ag_2CO_3 from the Fisher Scientific company, $PbCO_3$ (99 %) from the Park Scientific company and standard lead solution (1 g/L) from the Fluka company.

The pH values of the experimental solutions were adjusted to 4.0 with HNO_3 and NaOH. The solutions were adjusted to a constant ionic strength with KNO_3.

Standard reference materials

Bleizinn XVII: Sn (29.18 %), Pb (69.25 %), Sb (1.53 %) and Weissmetall V: Sn (39.91 %), Sb (5.85 %), Cu (0.55 %), Pb (53.53 %) were obtained from Dr Hoefner's Subztanz Company. Appropriate amounts of standard material were dissolved in HNO_3 with heating, filtered from blue band filter paper, and made up to 100 mL with deionized water.

2.3. Preparation of the electrode

The active phase of the solid-state electrodes is formed by sulfide, oxide, selenide and other salts of lead together with sulfide of other metals /4, 20, 41/. The membranes of the electrodes in this study were prepared by the use of two different methods. In the first method $PbCO_3$ (13.40 g), Ag_2CO_3 (13.80 g), elemental sulfur (20.00 g), Na_2CO_3 (2.00 g) and K_2CO_3 (10.00 g) were thoroughly mixed, placed in a fusion column and fused under nitrogen atmosphere by first subjecting to a low Bunsen flame until all the material was black and then a temperature around 600 °C by showing an utmost care for the homogeneity of the fusion process. As a result of fusion process which took around six hours a solid mixture of Pb(II)-Ag(I) sulfides was obtained as membrane material. The solid mass was abraded with a rotating file until a membrane in 1.2 cm diameter and 0.4 mm in thickness was obtained. A helical copper wire was glued to the internal surface of the disc shaped solid membrane ($PbS+Ag_2S$) with silver cement to provide electrical contact. The membrane was then mounted to the glass tube with an appropriate binder. There was no internal filling solution used.

The second method for the preparation of a solid-state membrane Pb(II) sensitive electrode was the precipitation of lead and silver sulfide in different beakers by the use of thioacetamide. The precipitates were washed with deionized water three times and dried off in air. The mass ratios of PbS to Ag_2S was changed as 9:1; 7:3; 6:4, 5:5 and they were mixed in a crucible.

The total mass of sulfide mixtures was 7.0 g. Then, 5.0 g NaCl was added to all sulfide mixtures to prevent them from air penetration. These mixtures were kept in an oven at a temperature of 900 °C for two hours, then the oven was turned off and the material was kept there until it cooled down to the room temperature. The samples were then treated with deionized water in order to remove the residual sodium chloride. The resulting solid was abraded with a rotating file to form a disc shape membrane mentioned above. The electrode prepared with this method was subjected to the same procedures to which the electrode prepared using the first method had been subjected.

2.4. Potential measurements

The cell used in the potential measurements was constructed with the use of Ag/AgCl as the double junction reference electrode Orion 9002 and the proposed lead-selective electrodes as the indicator electrode. The schematic representation of the electrochemical cell is as follows:

Ag/AgCl, KCl(sat)//test solution / (membrane)/ Copper wire

The electrode was conditioned in 1.0×10^{-3} M $PbNO_3$ solution for half an hour before being used in the experiments. The test solution was stirred with a magnetic stirrer and the potentials were recorded after the equilibrium potentials had been reached.

3. RESULTS AND DISCUSSION

3.1 Membrane composition

It is well known that the sensitivity and the selectivity obtained for a given ion-selective electrode depend not only the nature of the active material but also significantly on the membrane composition. Therefore, in the preliminary experiments, in order to determine the optimum conditions for the best performance of the Pb(II)-selective electrode, the solid-state membranes were prepared by two different methods. There was no considerable difference observed in the performances of the electrodes with the membranes prepared by the first and the second method. Hence, ease and speed of the membrane preparation caused us to prepare solid membranes by the second method. A number of membrane compositions were investigated by varying the ratio of PbS:Ag_2S. However, the composition of the membranes was found to affect the slope and the working range of electrodes. The results for the electrodes prepared by the second method are tabulated in Table 1.

The table shows that the best performance was obtained with the membrane containing 50 % PbS and 50 % Ag_2S and this membrane was used throughout the study.

Table 1

The effect of the membrane composition upon the performance of the lead(II)-selective solid-state membrane electrode

Membrane composition, (m/m%)	Slope of the electrode, mV/pPb	Working range, M
90 % PbS: 10 % Ag_2S	18.7 ± 0.2	1.0×10^{-1}- 1.0×10^{-4}
70 % PbS: 30 % Ag_2S	22.3 ± 0.4	1.0×10^{-1}- 1.0×10^{-4}
60 % PbS: 40 % Ag_2S	26.0 ± 0.6	1.0×10^{-1}- 1.0×10^{-5}
50 % PbS: 50 % Ag_2S	28.3 ± 0.2	1.0×10^{-1}- 1.0×10^{-5}

3.2. Effect of pH

The choice of appropriate pH range is of paramount importance for the accurate measurements /2, 4- 10, 12, 13, 15, 16/. According to the literature, most of the studies were carried out at acidic pH values /9, 10, 15- 17/. We examined the pH-dependence to determine the effective pH range for the electrode. The pH of the solutions was adjusted by adding appropriate amount of dilute nitric acid and sodium hydroxide solution. The ionic strength of the solutions was adjusted to 0.25 M KNO_3. The influence of pH was studied over the pH range of 2-9 at 1.0×10^{-3} M $Pb(NO_3)_2$ containing solutions. The potential was recorded against the pH value. As shown in Figure 1, we found that the potential of the electrode did not show an appreciable change in the pH range of 3.5-6.0. Outside this range, the electrode response changed drastically. The obtained changes of potential at lower (< pH 3.5) and higher (> pH 6.0) pH values could be attributed to the interference of hydrogen ion partially effecting the solubility of the membrane and precipitation of Pb(II) ions as hydroxides because of the increasing amount of sodium hydroxide, respectively /2, 9, 10, 18-20/. Therefore, in this study, the pH value was adjusted to 4.0 in all measurements.

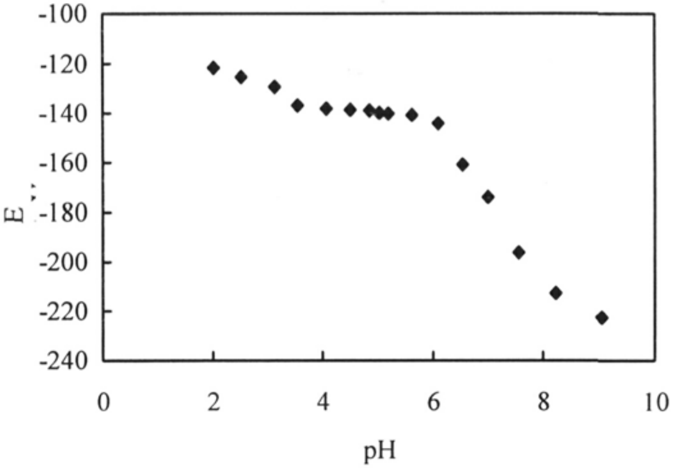

Fig. 1: The effect of pH of test solutions containing 1.0 × 10^{-3} M $PbNO_3$ on the response of the Pb(II)–selective solid-state electrode (50 % PbS: 50 % Ag_2S).

3. 3. Determination of the working range and the detection limit

The calibration curve of the lead-selective electrode was drawn by the use of $Pb(NO_3)_2$ solution at the concentrations between 1.0 × 10^{-1} M and 1.0 × 10^{-7} M. The ionic strength of the solutions was fixed to 0.25 M with KNO_3. The pH of the test solutions were adjusted to 4.0 by adding appropriate amount of dilute NaOH and HNO_3. The potential response of the proposed lead-selective electrode was measured against Ag/AgCl reference electrode. The measurements were made in the order of dilute solutions to concentrated ones. The potential values recorded for each solution were plotted against the concentration to obtain the calibration plot of the lead-selective electrode (Figure 2). The range and the slope of the linear portion of the graph were taken as the working range and the slope of the electrode.

The working range of the electrode prepared was found to be 1.0 × 10^{-1} - 1.0 × 10^{-5}M. The average slope obtained from five different responses of the electrode was found to be 28.2 ± 0.8 mV/pPb (R^2: 0.9938).

The value of 28.2 mV/pPb is very close to the Nernstian value. The detection limit of the electrode was found as 3.2×10^{-6} M from the intersection of two extrapolated segments of the calibration curve. These values show that the prepared electrode has a comparable working range and detection limit among some similar electrodes reported in literature /2, 32, 42/ and is much more better than many others /14, 17, 43, 44/.

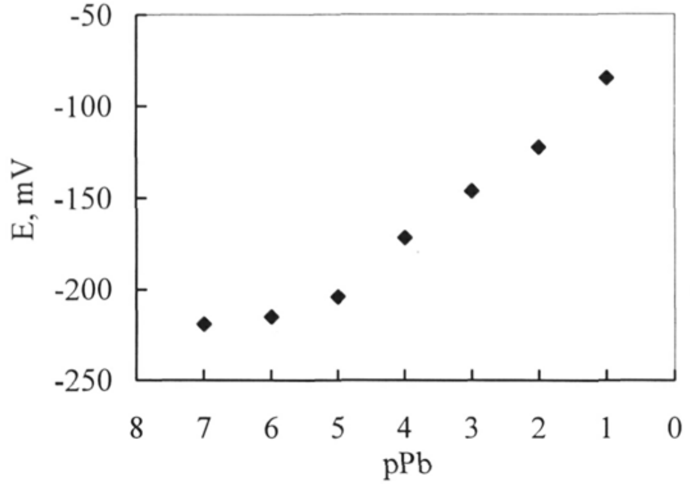

Fig. 2: Potential response of the lead-selective electrode (50 % PbS: 50 % Ag_2S).

3.4. Response time and the lifetime of the electrode

One of the most important performance characteristics of the ion-selective electrodes is the response time, which should be suitable for rapid method of analysis. For this purpose, the average time required for the Pb(II) ion sensor to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of lead(II) ion solutions, each having a 10-fold difference in concentration, was measured. It was highly affected by the change in the concentration of the test solutions. If the electrode conditioned in 1.0×10^{-3} M $PbNO_3$ solution was immersed in a solution with a concentration of 1.0×10^{-7} M $PbNO_3$, the response time was observed to be 20-25 s. But a response time of 5-10 s was obtained for concentrations $\geq 1.0 \times 10^{-5}$ M $PbNO_3$. The equilibrium potential remained constant for more than 8 min, after which only a slow divergence was reported. For the proposed electrode, the average response time was found to be 10-15 seconds. In conclusion, this value is comparable to and shorter than many of the similar electrodes reported in literature /10, 14, 15, 18, 43/.

The lifetime of the electrode was determined by measuring its potentials and plotting the calibration curves for a period of a year. The slope of the electrode was observed to show no significant change. As a result of routine measurements for 14 months, it could be said that the proposed electrode could be used for at least a year with no measurable divergence. However, the lifetimes of the similar Pb(II)-selective solid-state and neutral carrier based polymer membrane electrodes reported in the literature are much shorter than this period; they are limited to a few months /2, 10, 12, 13/.

3.5. Selectivity coefficients of the lead-selective electrode

The potentiometric selectivity coefficients are defined by the electrode's relative response for the primary ion over other ions present in the solution /45/. In this work, the selectivity coefficients of the electrode against Ag(I), Cu(II), Ca(II), Mg(II), Hg(II), Ni(II), K(I), Ba(II), Fe(II), Co(II), Cd(II), Zn(II) and Sr(II) ions were determined by the fixed interference method which is based on the Nicolsky-Eisenman equation recommended by IUPAC /46/. The concentration of the lead ion was varied in the concentration range of 1.0×10^{-1} - 1.0×10^{-7} M while that of the interfering ion was 1.0×10^{-3} M. The resulting selectivity coefficient values thus obtained for the proposed Pb(II)-selective electrode are given in Table 2. As can be seen, in most cases, the selectivity coefficients are on the order of 1.0×10^{-2}- 1.0×10^{-3}, which seems to indicate that these cations have negligible impact on the functionality of the Pb(II)-selective electrode. Almost all of the Pb(II)-selective electrodes in literature were reported to be strongly affected by the presence of the silver ions in the solution /2, 10, 17, 19, 20-24, 27, 28, 30, 42, 43/. The Pb(II)-selective electrode developed was also found to be highly affected by the presence of Ag(I) coming from the use of Ag_2S in membrane and Hg(II) in the solution. It is evident from most of the published reports that besides Ag(I) and Hg(II) ions, Cu(II), Ca(II) and Cd(II) ions are significantly interfering with the determination of Pb(II) ions too /10, 14, 21, 25-30, 43/. However, the results in Table 2 show that Cu(II), Ca(II), Cd(II) would not disturb the functioning of our electrode.

Table 2
The selectivity coefficients of the Pb(II)-selective electrode determined by using fixed interference method

Interfering ions	Selectivity coefficients, log $K_{Pb,M}^{pot}$
Ca^{2+}	-2.09
Co^{2+}	-2.52
Zn^{2+}	-2.70
Ni^{2+}	-2.00
Mg^{2+}	-2.70
Sr^{2+}	-2.52
Ba^{2+}	-2.00
Cd^{2+}	-1.30
Mn^{2+}	-3.00
Fe^{3+}	-3.00
Cu^{2+}	-1.20
Ag^{+}	Interfering ion
Hg^{2+}	Interfering ion

3.6. Analytical applications

The practical utility of the proposed electrode was tested by its use as an indicator electrode in the potentiometric titration of Pb(II) ions with EDTA. Bleizinn XVII, Weissmetall V standard materials and a standard lead solution (C: 1g/ L) were used to determine the amount of lead in the sample solutions. Appropriate amounts were taken from them and standard sample solutions were prepared at different lead concentrations. They were potentiometrically titrated with 0.02027 M EDTA solution at pH 4.0. First, the sample solution prepared from standard lead solution was titrated with EDTA and the recovery of the determinations was found to be 99.53 ± 1.43 % by using the proposed electrode. Then, the other sample solutions prepared from two standard materials were also potentiometrically titrated. An example of the titration curves is given below (Figure 3).

The presence of Sb(III), Sn(II) and Cu(II) ions in the standard materials' solutions caused no interfering effect. This confirmed that the electrode prepared could be successfully applied as an indicator electrode in potentiometric titrations of real samples.

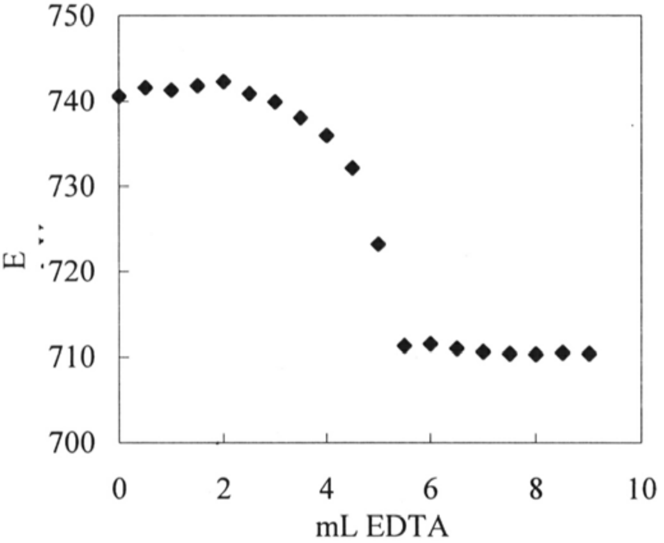

Fig. 3: Potentiometric titration curve of 5.0 mL of 2.0×10^{-1} M Pb(II) solution prepared from Weissmetall V standard material with 0.02027 M of EDTA at pH 4.0.

The lead contents of two standard reference materials were also determined by the use of commercial lead-selective electrode for comparative purposes. The related data are tabulated in Table 3. There were no statistically significant differences between the results obtained with the proposed lead-selective electrode and the commercial Pb(II)-selective electrode at confidence level of 95 %.

4. CONCLUSION

On the bases of the results discussed in this study, a new lead-selective solid-state membrane electrode was developed by using a new solid-state membrane preparation technique. The best performance was observed with a membrane composition of 50 % PbS-50 % Ag_2S. The proposed lead-selective solid-state membrane electrode gave satisfactory results with real samples and was found to work well under laboratory conditions. The fact that there

Table 3
Comparison of the proposed Pb(II)-selective electrode and the commercial Pb(II)-selective electrode

Standard samples, μ, Pb^{2+} %	Results obtained with the electrode proposed Pb %			Results obtained with the commercial electrode Pb %			Comparison of two electrodes
	$\overline{X_1} \pm \frac{t.s}{\sqrt{N}}$	S	N	$\overline{X_2} \pm \frac{t.s}{\sqrt{N}}$	S	N	$\left\|\overline{X_1} - \overline{X_2}\right\| < ts_b\sqrt{\frac{N_1 + N_2}{N_1 \times N_2}}$
Weissmetall V, 53.53	53.14 ± 1.23	± 0.99	5	52.74 ± 2.75	± 2.21	5	0.40 < 2.50
Bleizinn XVII, 69.25	68.95 ± 0.37	± 0.30	5.	68.87 ± 0.51	± 0.41	5	0.08 < 0.53

was no interfering effect observed with tin, antimony and copper ions showed that the electrode could be used in real samples. In determinations carried out with different Pb(II) concentrations and matrices, the relative error was found to be less than 2 %. The potentiometric determinations made with EDTA revealed the fact that the electrode developed could be successfully employed as an indicator electrode. When compared with the similar electrodes reported in literature, offering advantages such as speed and ease of preparation and procedures, the prolonged lifetime, Pb(II)-selective electrode proposed here can also be constructed for commercial purposes.

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